ARMY RESEARCH LABORATORY

Producing Known Quantities of RDX for LIBS Limit of Detection Study

by Frank C. De Lucia, Jr.

ARL-TR-6002 **May 2012**

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory
Aberdeen Proving Ground, MD 21005

ARL-TR-6002 **May 2012**

Producing Known Quantities of RDX for LIBS Limit of Detection Study

Frank C. De Lucia, Jr.
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
May 2012	Final	

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Producing Known Quantities of RDX for LIBS Limit of Detection Study	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Frank C. De Lucia, Jr.	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army Research Laboratory ATTN: RDRL-WML-A Aberdeen Proving Ground, MD 21005	ARL-TR-6002

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Laser induced breakdown spectroscopy (LIBS) is an optical elemental analysis technique that has shown promise for detecting trace amounts of explosive residue. The need to quantify the detection limits for explosives using LIBS is an important step for determining the effectiveness of the LIBS technique, and requires the ability to produce known amounts of explosives reproducibly. To that end, we have employed an inkjet printing system to produce samples with a range of known amounts of trace explosives (sub 100 nanograms.) The detection limits were determined based on the relationship between the LIBS spectral data and the mass of the explosive. Based on this proof of principle study, preliminary detection limit results were found to be ~1.5 and ~0.1 ng for two different laser energies using this particular experimental configuration.

15. SUBJECT TERMS

LIBS, quantifiable, limit of detection, trace explosives, detection

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Frank C. De Lucia, Jr.
Unclassified	Unclassified	Unclassified	UU	18	19b. TELEPHONE NUMBER (*Include area code*) 410-306-0884

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures

List of Tables

1. Introduction

The ability to detect trace explosives is of interest to the U.S. Army Research Laboratory (ARL). The presence of small amounts of explosives could be an indicator of a larger explosive nearby, either an improvised explosive device (IED) or a homemade explosive (HME). At ARL, we have been investigating the possibility of using standoff laser induced breakdown spectroscopy (LIBS) as a method to detect trace explosives at a distance (*1–4*). We have demonstrated the feasibility of classifying unknown trace residues as either explosives or non-explosives on a variety of surfaces (*5*). For ongoing studies, we need to be able to quantify the amounts of explosives interrogated by the LIBS microplasma. The ability to produce known, relevant amounts of explosive on a variety of surfaces is needed. A 2006 Massachusetts Institute of Technology (MIT) Lincoln Laboratory study measured the amount of explosives left on surfaces by an individual who was handling explosives (*6*). By applying a known range of explosive quantities, the detection limit of different trace explosive detection methods can be determined. In order to produce these known, relevant amounts of trace explosives, we used an inkjet printing system (JetLab 4, MicroLab Systems). In this report, we performed a proof-of-principle experiment using the inkjet printer to produce a range of known cyclotrimethylene-trinitramine (RDX) quantities onto aluminum (Al) substrates. These samples were interrogated by a bench top LIBS system in order to calculate a detection limit. The procedure for producing known quantities of relevant amounts of explosives and determining the detection limit can then be applied to different LIBS systems or other explosive detection methods for a variety of trace detection applications.

2. Experiment

Colleagues at ARL provided the RDX that was used in the experiment. The RDX was dissolved into the solvent isobutanol at a concentration of ~0.4 mg/mL. The solution was then filtered through a membrane with a pore size of 0.45 μm so that no large RDX particulate would clog the inkjet nozzle. The concentration of the resulting solution was determined by adding known quantities of the solution to weighing dishes. The isobutanol was allowed to evaporate, and then the RDX was weighed. The concentration of the solution was determined to be 0.18 ± 0.02 mg/mL. The inkjet system is shown in figure 1. The RDX solution was placed in the inkjet reservoir. The inkjet produces a defined number of small droplets (~100 pL per droplet) that are deposited onto a substrate in a predetermined pattern. The droplet evaporates, depositing the solute onto the substrate surface. The inkjet system is used to calculate the average volume of the droplets.

Figure 1. Jetlab 4 (MicroFab systems).

Samples were prepared by dropping 100 droplets on a position on an Al substrate. Then the inkjet nozzle moved to a different spot and dropped another 100 droplets. This procedure was repeated until a 5 × 4 grid of RDX deposits had been formed. The process is repeated by dropping another 100 droplets at each point on the grid. This is repeated until the desired number of droplets is reached at each point of the grid. By adding 100 drops at a time to each sample spot on the grid, we produced uniform-sized deposits of different quantities. The size of the RDX deposited on the Al was a small ring less than a millimeter in diameter that was consumed entirely by a single laser-generated microplasma. For this experiment, we produced nine samples with RDX deposited in a 5 × 4 grid. The first substrate had 200 drops deposited at each grid point. The second substrate had 300 drops deposited at each grid point, and so forth, up to the ninth substrate, which had 1000 drops deposited at each grid point. From the number of droplets, the droplet volume, and the sample concentration, the deposited mass of RDX was calculated.

The LIBS system experimental setup is shown in figure 2. A neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Big Sky, CFR400) produces a nanosecond laser pulse that was focused by a 10 cm focal length lens onto the sample surface and fired in a single-shot mode. The emission from the resulting microplasma was collected by a parabolic mirror and focused onto a seven-fiber (600 μm diameter) bundle. Each fiber was connected to one of the seven channels in the multi-channel charge-coupled device (CCD) spectrometer (Ocean Optics Inc., LIBS 2000+), giving broadband coverage from 200–950 nm at relatively high resolution (~0.1 nm). The spectrometer was set to begin collecting light 1.00 μs after the plasma initiation in order to reduce the background continuum inherent in LIBS experiments. The spectrometer gate width was 2 ms. An argon (Ar) flow was directed across the sample surface where the microplasma was formed to minimize the oxygen (O) and nitrogen (N) contributions from air.

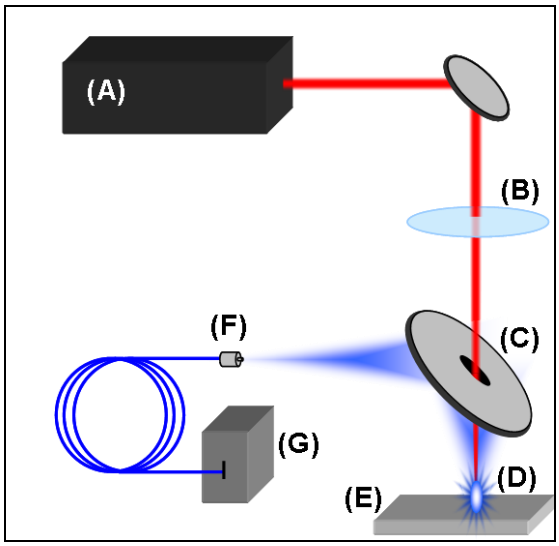

Figure 2. LIBS experimental setup (a) Nd:YAG laser, (b) focusing optics, (c) pierced mirror, (d) microplasma, (e) sample, (f) collection optics, and (g) spectrometer/detector.

3. Results

Two sets of samples were produced in order to determine the detection limit for RDX on Al for two different laser energies, 230 and 340 mJ. The two sample sets are shown in table 1. Twenty LIBS spectra were collected from each sample. Representative spectra from the Al substrate blank, the 300 drop sample, and the 700 drop sample collected at 340 mJ are shown in figure 3. The largest atomic emission lines are due to the Ar bath gas and the Al substrate. We are only interested in the atomic emission lines associated with the constituent elements of RDX—i.e., carbon (C), hydrogen (H), O, and N—shown in the insets. As more drops are applied, we see the atomic emission intensities of C, H, N, and O increase, indicating that more RDX is present as more drops from the inkjet printer are applied. The strongest atomic C emission line is shown in the top left inset of figure 3. We used the atomic emission line intensity at 247.8 nm to calculate the detection limit of RDX on Al. The standard deviation of the noise was first calculated. Any individual C emission intensity at 247.8 nm that was not three times the standard deviation of the noise was considered to not have a significant C signal and was set to zero. The average background corrected C emission intensity at 247.8 nm was calculated from the 20 samples. We removed any samples that had a C emission intensity outside of two standard deviations from the average. From the remaining spectra, we kept the 10 that had the largest emission intensities. We then recalculated the C intensity average from the 10 spectra. This process was repeated for each set of samples, and the results are displayed in table 1. In figure 4, the C intensity is

displayed as a function of mass for the samples collected using a 230-mJ laser pulse. A linear fit and a weighted linear fit are applied to the data points. The limit of detection can be determined from the linear fits in figure 4 by the following equation

$$L.O.D. = \frac{3 * \sigma_b}{m} \ , \qquad (1)$$

where σ_b is the standard deviation of the noise at 247.8 nm on the blank Al substrate, and m is the slope of the line. The slope defines the analytical sensitivity of the measurements. Using equation 1 and the data from figure 4, we calculated the detection limit of RDX on Al using a 230-mJ laser pulse as **1.42 ± 0.08 ng** for the linear fit and **1.64 ± 0.09 ng** for the weighted linear fit. The same process was repeated for the LIBS spectra collected using 320 mJ. Using equation 1, the detection limit of RDX on Al using a 320-mJ laser pulse was found to be **0.12 ± 0.01** and **0.17 ± 0.02 ng** for the linear and weighted linear fits, respectively.

Table 1. Quantifiable RDX samples used to determine the detection limit of the LIBS system at two laser energies.

RDX Samples Collected With 230 mJ			
No. of Drops	**Average Drop Volume (pL)**	**Mass (ng)**	**Carbon Intensity**
0 (blank)	0	0	0
200	135 ± 8	4.8 ± 0.6	16 ± 2
300	122 ± 7	6.6 ± 0.8	19 ± 3
400	150 ± 10	10.8 ± 1.4	22 ± 3
500	134 ± 11	12.1 ± 1.7	18 ± 4
600	137 ± 5	14.8 ± 1.7	42 ± 10
700	140 ± 5	17.6 ± 2.1	57 ± 20
800	148 ± 10	21.3 ± 2.7	62 ± 10
900	138 ± 10	22.4 ± 2.9	65 ± 13
1000	146 ± 7	26.3 ± 3.2	89 ± 9
RDX Samples Collected With 340 mJ			
0 (blank)	0	0	0
300	104 ± 9 (measured once and used for all the following samples)	5.6 ± 0.8	88 ± 30
400	“	7.5 ± 1.1	198 ± 41
500	“	9.4 ± 1.3	447 ± 80
600	“	11.2 ± 1.6	516 ± 94
700	“	13.1 ± 1.8	571 ± 102

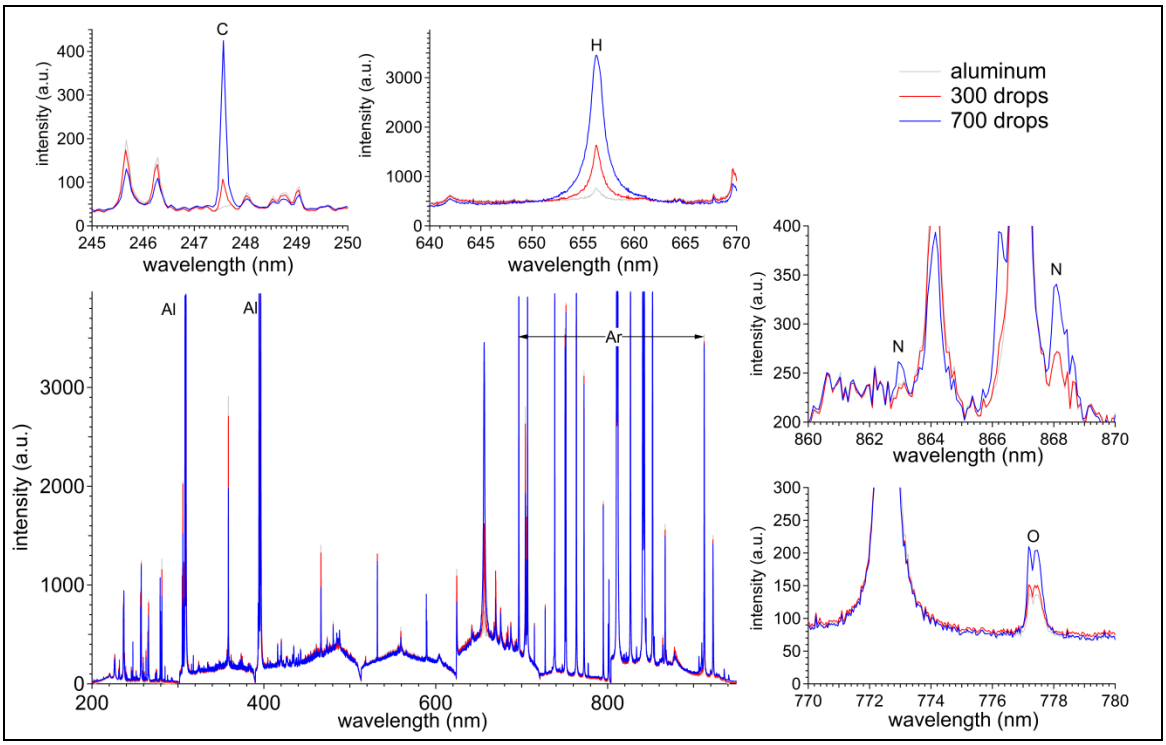

Figure 3. LIBS spectra of blank Al, RDX deposit from 300 drops, and RDX deposit from 700 drops. Insets show C, H, N, and O atomic emission lines.

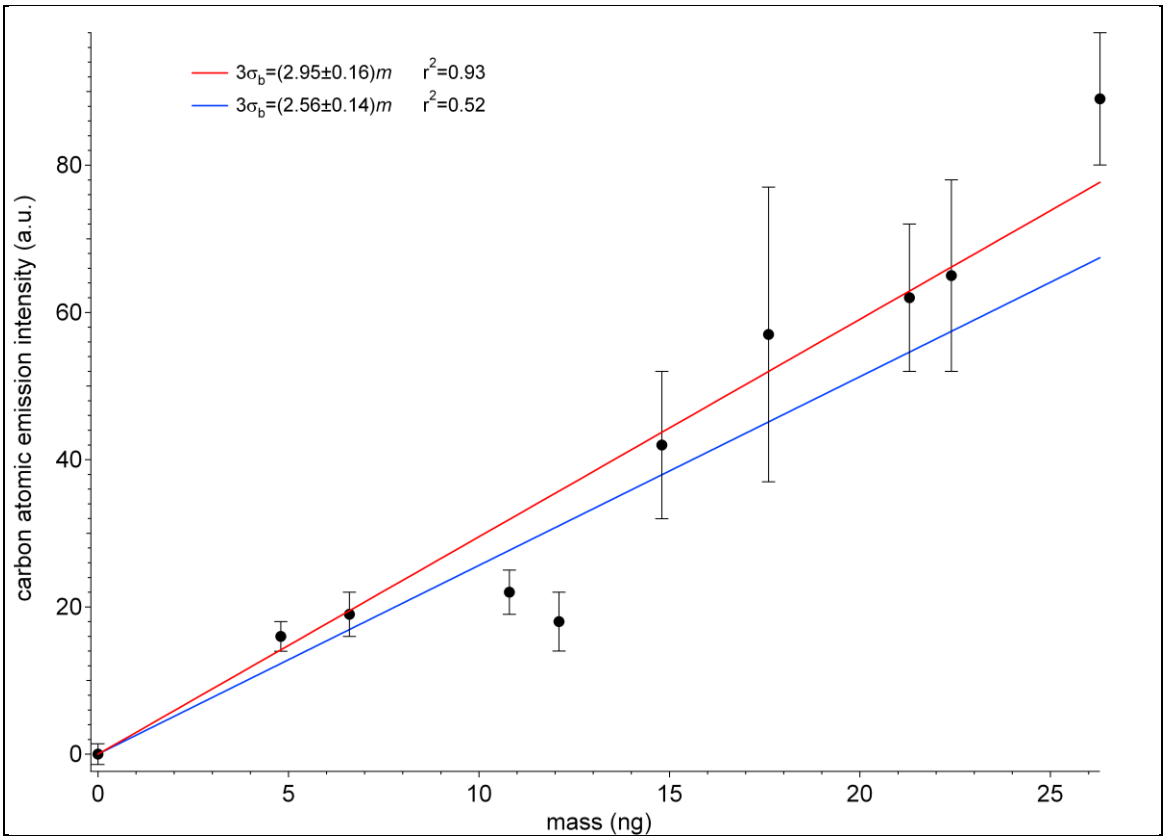

Figure 4. C atomic emission intensity as a function of the mass of RDX. A linear fit (red) and a weighted linear fit (blue) were used to fit the data. Error bars represent one standard deviation.

4. Conclusion

We have established a procedure for creating quantifiable explosive samples that can be tested with LIBS systems and other trace explosive detectors in order to determine the limit of detection. The inkjet printer will allow samples to be made on all kinds of surfaces and is not limited to Al. Different surfaces will interact with the droplets in different ways, so care must be made in observing how the droplets interact with the surface and how the deposit is drying. This is important for LIBS because an assumption is made that the sample is entirely consumed by the microplasma. If the sample has spread over a larger area than the microplasma sampling area, the detection limit calculation will not be accurate. We also demonstrated that the detection limit is dependent on laser energy. The microplasma generated by the 340-mJ laser energy consumed and ionized the RDX deposit more efficiently than the 230-mJ laser pulse; therefore, the signal-to-noise due to the C atomic emission line increased. The detection limit would also be significantly altered by changing the substrate because the LIBS emission signal is dependent on the laser-material interaction.

We used a linear fit and a weighted linear fit to determine the detection limits from the C intensity as a function of RDX mass. The weighted linear fit returns a much lower R^2 value since it is dependent on the standard deviation of the C intensity at each mass value. Using a weighted linear fit is more statistically sound; for this present experiment, however, only 10 samples were used for each mass amount. To improve future experiments, more samples must be obtained in order to provide a more robust statistical quantification. Improvement to the linear fit could also be obtained by selecting an appropriate internal standard. In the case of this experiment, the internal standard could be an Ar atomic emission line, or an atomic emission line associated with the Al substrate. A good internal standard choice would be an atomic line that has a similar emission wavelength and upper energy state to the analyte atomic emission line (*7*).

For this particular experiment, we calculated detection limits of 0.12 and 1.42 ng using a linear fit at laser energies of 340 and 230 mJ, respectively. The calculated detection limits only apply to this particular LIBS setup—i.e., focusing and collecting optics configurations, the detector, Ar bath gas, and Al substrate. Further improvements that could be made to the procedure include selecting a wider range of deposition quantities in order to obtain a better indication of the dynamic range of the detection method. The use of double pulse LIBS could further improve the detection limit since the two pulses would increase the signal by more efficiently ionizing the sample (*8, 9*). Finally, multivariate analysis could be used by using more of the LIBS spectral signal for determining the detection limit. Other atomic emission lines from the constituent elements (C, H, O, and N) beyond the C atomic emission line at 247.8 nm would be incorporated into the quantification analysis.

5. References

1. Gottfried, J. L.; De Lucia, Jr., F. C.; Munson, C. A.; Miziolek, A. W. Double-Pulse Standoff Laser-Induced Breakdown Spectroscopy for Versatile Hazardous Materials Detection. *Spectrochimica Acta Part B: Atomic Spectroscopy* **2007**, *62* (12), 1405–1411.

2. De Lucia, Jr., F. C.; Gottfried, J. L.; Munson, C. A.; Miziolek, A. W. Multivariate Analysis of Standoff Laser-Induced Breakdown Spectroscopy Spectra for Classification of Explosive-Containing Residues. *Applied Optics* **2008**, *47* (31), G112–G121.

3. Gottfried, J. L.; De Lucia Jr., F. C.; Munson, C. A.; Miziolek, A. W. Strategies for Residue Explosives Detection Using Laser-Induced Breakdown Spectroscopy. *Journal of Analytical Atomic Spectrometry* **2008**, *23*, 205–216.

4. De Lucia, Jr., F. C.; Gottfried, J. L.; Munson, C. A.; Miziolek, A. W. Current Status of Standoff LIBS Security Applications at the U.S. Army Research Laboratory. *Spectroscopy* **2009**, *24* (6), 1.

5. Gottfried, J. L.; De Lucia, Jr., F. C.; Miziolek, A. W. Discrimination of Explosive Residues on Organic and Inorganic Substrates Using Laser-Induced Breakdown Spectroscopy. *Journal of Analytical Atomic Spectrometry* **2009**, *24* (3), 288–296.

6. Kunz, R. R.; Hybl, J. D.; Pitts, J. D.; Switkes, M.; Herzig-Marx, R.; Leibowitz, F. L.; Williams, L.; Worsnop, D. R. *Measurement of Explosive Residues Associated With Assembly and Deployment of IEDs*; 81–1004; Massachusetts Institute of Technology Lincoln Laboratory: Lexington, Massachusetts, 14 February 2006.

7. Zhang, L.; Dong, L.; Dou, H.; Yin, W.; Jia, S. Laser-Induced Breakdown Spectroscopy for Determination of the Organic Oxygen Content in Anthracite Coal Under Atmospheric Conditions. *Applied Spectroscopy* **2008**, *62* (4), 458–463.

8. Babushok, V. I.; De Lucia, Jr., F. C.; Gottfried, J. L.; Munson, C. A.; Miziolek, A. W. Double Pulse Laser Ablation and Plasma: Laser Induced Breakdown Spectroscopy Signal Enhancement. *Spectrochimica Acta Part B* **2006**, *61*, 999–1014.

9. Cristoforetti, G.; Legnaioli, S.; Palleschi, V.; Salvetti, A.; Tognoni, E. Characterization of a Collinear Double Pulse Laser-Induced Plasma at Several Ambient Gas Pressures by Spectrally- and Time-Resolved Imaging. *Applied Physics B: Lasers And Optics* **2005**, *80* (4–5), 559–568.

List of Symbols, Abbreviations, and Acronyms

Al	aluminum
Ar	argon
ARL	U.S. Army Research Laboratory
C	carbon
CCD	charge-coupled device
H	hydrogen
HME	homemade explosive
IED	improvised explosive device
LIBS	laser induced breakdown spectroscopy
MIT	Massachusetts Institute of Technology
N	nitrogen
Nd:YAG	neodymium-doped yttrium aluminum garnet
O	oxygen
RDX	cyclotrimethylene-trinitramine

NO. OF COPIES	ORGANIZATION
1 PDF	DEFENSE TECH INFO CTR ATTN DTIC OCA (PDF) 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	DIRECTOR US ARMY RSRCH LAB ATTN IMNE ALC HRR MAIL & RECORDS MGMT 2800 POWDER MILL ROAD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RSRCH LAB ATTN RDRL CIO LL TECHL LIB 2800 POWDER MILL ROAD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RSRCH LAB ATTN RDRL CIO LT TECHL PUB 2800 POWDER MILL ROAD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RSRCH LAB ATTN RDRL SEE O P PELLEGRINO 2800 POWDER MILL ROAD ADELPHI MD 20783-1197

NO. OF COPIES	ORGANIZATION
1	EDGEWOOD CHEMICAL BIOLOGICAL CENTER ATTN RDCB DPC MT C A POORE 5183 BLACKHAWK RD BLDG E5830 ABERDEEN PROVING GROUND MD 21010-5424
1	FOREIGN MILITARY STUDIES OFFICE ATTN C HURST 731 MCCLELLAN AVE FORT LEAVENWORTH KS 66027
1	NATIONAL GROUND INTELLIGENCE CENTER ATTN D BARLOW 2055 BOULDERS RD CHARLOTTESVILLE VA 22911-8318
1	PM-IED DEFEAT/PROTECT FORCE ATTN A Z VILLAR BUFFINGTON RD BLDG 183 PICATINNY ARSENAL NJ 07086-5000
1	US ARMY CRIMINAL INVESTIGATION LAB ATTN J SALYARDS 4930 N. 31ST ST FOREST PARK CA 30297
1	US ARMY NIGHT VISION AND ELECT SENSORS DIRECT ATTN RDER NVS CT D PINKHAM 10221 BURBECK RD FT BELVOIR VA 22060-5806
1	NAVAL RSRCH LAB ATTN J SEELY 4555 OVERLOOK AVE SW WASHINGTON DC 20375-5352
1	NAVEODTECHDIV ATTN CODE 5122 D LEE 2008 STUMP NECK RD BLDG 2172 INDIAN HEAD MD 20640
1	NAVEODTECHDIV ATTN CODE 5122 D RODDY 008 STUMP RD BLDG 2172 INDIAN HEAD MD 20640
1	FEDERAL BUREAU OF INVESTIGATION WMD COUNTERMEASURES UNIT ATTN D S BEREZANSKY 935 PENNSYLVANIA AVE NW WASHINGTON DC 20535
1	IDAHO NATIONAL LABORATORY ATTN R FOX PO BOX 1625 IDAHO FALLS ID 83415-2208
1	LAWRENCE BERKLEY NATIONAL LABORATORY ATTN R RUSSO 1 CYCLOTRON RD MAILSTOP 70R0108B BERKLEY CA 94720
1	US DEPARTMENT OF HOMELAND SECURITY ATTN R P JOHNS WASHINGTON DC 20528
1	US DEPARTMENT OF HOMELAND SECURITYVFEMA ATTN W YODER 16825 S SETON AVE EMMITSBURG MD 21727
1	FLORIDA INTERNATIONAL UNIVERSITY ATTN J ALMIRALL 11200 SW 8 ST MIAMI FL 33199
1	UNIVERSITY OF CENTRAL FLORIDA ATTN M RICHARDSON 4000 CENTRAL FLORIDA BLVD ORLANDO FL 32816-2700

NO. OF COPIES	ORGANIZATION
1	UNIVERSITY OF NEBRASKA ATTN D ALEXANDER 209N WALTER SCOTT ENGR. CENTER PO BOX 880511 LINCOLN NE 68588-0511
1	BATTELLE BATTELLE EASTERN SCI AND TECHNOLOGY CENTER ATTN J ONTIVEROS 1204 TECHNOLOGY DR ABERDEEN MD 21001-1228
1	BATTELLE EAST SCI & TECH ATTN A ELLIS 1204 TECHNOLOGY DR ABERDEEN PROVING GROUND MD 21001-1228
1	GENERAL DYNAMICS ATTN N A MESSINA FOUR LAKEPOINT PLAZA 2118 WATER RIDGE PKWY CHARLOTTE NC 28217
1	LOCKHEED MARTIN ATTN S FREY 5600 SAND LAKE RD MP-450 ORLANDO FL 32819-8907
1	RAYTHEON INTEGRATED DEFENSE SYSTEMS ATTN R A MORO, JR 50 APPLE HILL DR TEWKSBURY MA 01876
1	SMITHS DETECTION ATTN D SCHIERING 21 COMMERCE DR DANBURY CT 06810
6	ARMY RSRCH LAB ATTN RDRL WML A A W MIZIOLEK ATTN RDRL WML B J GOTTFRIED ATTN RDRL WML C K L MCNESBY ATTN RDRL WML A C MUNSON ATTN RDRL WM B FORCH ATTN RDRL WML A W OBERLE ABERDEEN PROVING GROUND MD 21005
TOTAL	35 (34 HCS, 1 PDF)